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**(54) COMPOSITION FOR METAL SURFACE  
TREATMENT**

**(57) Abstract**

**PURPOSE:** To produce a composition for metal surface treatment having preventive performance of chromium elution and high corrosion resistance performance by combining and selecting emulsion contg. carboxylic acid and hydroxyl group of the specified composition, water soluble chromium compounds, water base colloid of inorganic compounds and inorganic compounds which reacts with amphoteric metal to form a water hardly soluble salt.

**CONSTITUTION:** Emulsion where an organic polymer consisting of 0.1-10wt.% ethylene base unsaturated

carboxylic acid components (acrylic acid, etc.), 1-30wt.% hydroxyl group contg. monomer components [2-hydroxyethyl (meta) acrylate, etc.] and 60-98.9wt.% other ethylene base unsaturated compounds (styrene, etc.) are stably dispersed in a water medium, water soluble chromium compounds (sodium chromate, etc.), water base colloid of inorganic compounds ( $\text{SiO}_2$  colloid, etc.) and inorganic compounds (phosphoric acid, etc.) which are reacted with amphoteric metal (Zn, Al) to a form a water hardly soluble salt are mixed as essential components. Thereby a composition giving a surface treatment film excellent in fingerprint resistance and wear resistance is obtained.

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CLAIMS

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[Claim(s)]

[Claim 1] (a) Ethylene system unsaturated-carboxylic-acid component = 0.1 - 10-% of the weight hydroxyl-group content monomer component The ethylene system unsaturated compound of =1 - 30-% of the weight others = constituent for metal finishing which comes to mix the inorganic substance with which the organic polymer which becomes at 60 - 98.9 % of the weight reacts with the organic polymer aqueous emulsion and (b) water solubility chromium compound which were distributed to stability, and the drainage system colloid of the (c) inorganic compound and the (d) amphoteric metal, and forms a difficult water solubility salt into an aqueous medium.

[Claim 2] It sets to (a) and other ethylene system unsaturated compounds are methacrylic acid alkyl ester and/or acrylic-acid alkyl ester. : 25 - 98.9 % of the weight, and other vinyl compounds : Constituent for metal finishing according to claim 1 with which it is 0 - 73.9 % of the weight, and glass transition temperature of (a) is characterized by -15-degree-C or more being less than 30 degrees C.

[Claim 3] The constituent for metal finishing according to claim 2 characterized by for the weight rate of the solid content of (a) and the solid content of (b) being 60:1 to 10:1, and the solid content concentration of (a) occupied in the constituent for metal finishing being more than 150g / lt.

[Claim 4] The constituent for metal finishing according to claim 3 characterized by for the weight rate of the solid content of (a) and the solid content of (d) being 20:1 to 1:1, and the weight rate of the solid content of (a) and the solid content of (c) being 30:1 to 1:1.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the constituent for metal finishing used for a non-painted application or a paint application.

[0002]

[Description of the Prior Art] Various kinds of chemical conversion for raising the corrosion resistance and adhesion over the base of zinc system plating, aluminum, iron which are used for an automobile, home electronics, and a building-materials application has been performed. The spreading mold chromate treatment of the non rinse which is not washed in cold water in it attracts attention, and is used. However, in conventional spreading mold KUROME-TO, in order to discover advanced corrosion resistance, many water-soluble chromium compounds had to be used, and there was a problem that chromium was eluted at the time of the nakedness activity of a chromate treatment steel plate, electrodeposition coating, or the cleaning processing before paint. This is the serious problem of environmental pollution, the need for chromium recovery-system installation, and the poor electrodeposition coating cause.

[0003] The approach of making compound hexavalent chromium with the approach and the organic polymer which are returned to trivalent with the reducing agent beforehand to the problem of such chromium elution, and fixing chromium, and the approach of covering an organic polymer further on a chromate film can be considered. For example, about immobilization of the chromium by organic polymer resin, there are JP,61-23767,A, JP,63-96275,A, and JP,63-175078,A. It is insufficient although hexavalent chromium and the mixing stability of each resin being improved with the carboxylic acid in resin in JP,61-23767,A and high corrosion resistance are found out, chromium elution cannot be prevented, but reduction of the chromium by the hydroxyl group in resin is proposed in JP,63-96275,A, and elution of chromium is simply prevented only in the property of a hydroxyl group.

[0004] The corrosion-resistant improvement by chromium has the large place depended on the sacrifice anticorrosive operation by elution of chromium. Therefore, returning the hexavalent chromium of elution nature beforehand, in order to press down chromium elution cannot deny corrosion-resistant lowering, preventing even it cannot be finished and it is not [ chromium elution ] enough. [ of adhesion and fingerprint-proof nature ] moreover -- the approach by reduction of the chromium by reducibility organic polymers, such as the conventional hydroxyl group, -- a moisture powder type or own stability of a water-soluble mold organic polymer -- bad -- becoming -- in addition -- and the elution prevention engine performance of chromium is low. About JP,63-175078,A, the description about an organic polymer is indefinite and chromium elution prevention ability is not certain, either.

[0005] moreover, the increment in cost accompanying the increment in a process in the approach by organic polymer coat -- happening -- in addition -- and the chromium elution from the breakage part and cutting part of this coat coat is a problem, and there are problems, such as also spoiling weldability.

[0006]

[Problem(s) to be Solved by the Invention] The object of this invention is to offer the constituent for

metal finishing which gives the surface treatment coat which can prevent elution of chromium upwards, with high corrosion resistance held, and was excellent also in fingerprint-proof nature and abrasion resistance.

[0007]

[Means for Solving the Problem] The object of this invention mentioned above A (a) ethylene system unsaturated-carboxylic-acid component = 0.1 - 10-% of the weight hydroxyl-group content monomer component The ethylene system unsaturated compound of 1 - 30-% of the weight others = = The organic polymer aqueous emulsion and (b) water solubility chromium compound which the organic polymer which becomes at 60 - 98.9 % of the weight distributed to stability in the aqueous medium, (c) It is attained more suitable for the constituent for metal finishing which comes to mix the drainage system colloid of an inorganic compound, and the inorganic substance which reacts with the (d) amphoteric metal and forms a difficult water solubility salt.

[0008] This invention carries out header attainment of the ability to be able to discover the engine performance with both the means of making a kind of reaction to which a water-soluble chromium compound, and said carboxylic-acid radical and hydroxyl group involve at the time of the desiccation and welding on the processed surface of metal of the organic polymer aqueous emulsion containing a carboxylic-acid radical and a hydroxyl group cause, in order [ both ] to satisfy both opposite engine performance [ say / the high chromium elution prevention engine performance and the high corrosion resistance ability which are the object ].

[0009] Hereafter, the detail of the constituent for metal finishing concerning this invention is explained. The organic polymer of the a. organic polymer aqueous emulsion in the constituent for metal finishing of this invention (only henceforth an invention constituent) uses an ethylene system unsaturated-carboxylic-acid component and a hydroxyl-group content monomer component as an indispensable component, and the remainder becomes with other ethylene system unsaturated compounds. About an ethylene system unsaturated-carboxylic-acid component, it is the copolymerization rate (based on the AUW of all the monomers that constitute this organic polymer.). the following -- setting -- being the same -- it is required to be 0.1 - 10% of the weight of within the limits, and it is 2 - 7 % of the weight preferably.

[0010] In adhesion with the top coat to a surface-of-metal [ which receives processing of an invention constituent ], and invention constituent coat top becoming inadequate when the copolymerization rate of this indispensable component is less than 0.1 % of the weight and exceeding 10 % of the weight, the membrane formation nature of an invention constituent coat falls, and it produces a problem in abrasion resistance etc. As an ethylene system unsaturated-carboxylic-acid component, although ethylene system partial saturation dicarboxylic acid, such as ethylene system partial saturation monocarboxylic acid, such as an acrylic acid, methacrylic acid, and a crotonic acid, an itaconic acid, a maleic acid, and boletic acid, those carboxylic-acid alkali-metal salts and ammonium salt, and an organic amine salt can be used, for example, they are an acrylic acid and methacrylic acid preferably.

[0011] About a hydroxyl-group content monomer component, the copolymerization rate needs to be 1 - 30% of the weight of within the limits, and it is 3 - 20 % of the weight preferably. If reactivity with the water-soluble chromium compound mentioned above, a carboxylic-acid radical, and a hydroxyl group cannot become inadequate, and elution of chromium cannot fully be prevented, when the copolymerization rate of this indispensable component is less than 1 % of the weight, and it exceeds 30 % of the weight, a reaction will advance superfluously in an invention constituent, and when spoiling the stability of liquid -- an invention constituent gels before processing to a surface of metal -- corrosion-resistant lowering is also produced.

[0012] As a hydroxyl-group content monomer component, acrylic-acid (meta) 2-hydroxyethyl, Acrylic-acid hydroxypropyl, acrylic-acid (meta) 3-hydroxy butyl, (Meta) An acrylic acid 2, 2-bis (hydroxymethyl) ethyl, an acrylic acid (meta) 2, 3-dihydroxy propyl, Acrylic-acid (meta) hydroxy ester, such as acrylic-acid-3-Krol-2-hydroxypropyl, (Meta) The monomer containing the reducibility hydroxyl group of alcoholic amides, such as allyl alcohol and N-methylol acrylamide, and N-butoxy methylol (meta) acrylamide, And the glycidyl (meta) acrylate which can expect the same reactivity as a hydroxyl

group in acid liquid, Although the monomer which has aldehyde groups which have glycidyl groups, such as allyl-glycidyl-ether, beta-methyl glycidyl (meta) acrylate, 3, and 4-epoxycyclohexylmethyl (meta) acrylate, such as a monomer and an acrolein, can be used They are acrylic-acid 2-hydroxyethyl and methacrylic acid 2-hydroxyethyl especially preferably. In addition, - expresses acrylic-acid (meta) and methacrylic acid - and/or acrylic-acid -.

[0013] It is old explanation, and although the organic polymer of this invention has a carboxylic-acid component and a hydroxyl-group component, 60 - 98.9 % of the weight of the remainders other than these components is other ethylene system unsaturated compounds. These compounds are ethylene system unsaturated compounds other than instantiation of the ethylene system unsaturated-carboxylic-acid component mentioned above and a hydroxyl-group content monomer component, and are methacrylic acid alkyl ester and/or acrylic-acid alkyl ester, i.e., (meta), acrylic-acid alkyl ester, and other vinyl compounds.

[0014] (Meta) As acrylic-acid alkyl ester, one sort chosen from alkyl ester, such as a methyl acrylate (meta), an ethyl acrylate (meta), butyl acrylate (meta), acrylic-acid (meta) hexyl, 2-ethylhexyl acrylate (meta), acrylic-acid (meta) octyl, acrylic-acid (meta) lauryl, acrylic-acid (meta) stearyl, acrylic-acid (meta) cetyl, acrylic-acid (meta) dodecyl, and acrylic-acid (meta) phenyl, or two sorts or more can be used.

[0015] Moreover, although one sort or two sorts or more of aromatic series vinyl compounds chosen from styrene, alpha methyl styrene, dimethylamino styrene, dimethylamino styrene (meta) acrylamide, vinyltoluene, chloro styrene, etc. are recommended especially as other vinyl compounds, compounds other than an aromatic series vinyl compound which carry out the following can also be used.

[0016] As others, for example Namely, methacryloiloxy-ethyl trimethylammonium chloride, Quarternary ammonium salt which is guided from an acrylic acid like 2-hydroxy-3-metacryloxy propyl trimethylammonium chloride (meta), The acrylic ester which has the third class amino group like acrylic-acid diethylamino ester, (Meta) And those quarternary ammonium salt, acrylamide (meta), dimethyl acrylamide, The monomer which has amino groups, such as acryloyl morpholine, an acrylic acid (meta) and quarternary ammonium salt guided from the amide amine obtained from diamine, Acrylic-acid triethylene glycol ester, the ester of the polyethylene glycol of an acrylic acid and polypropylene glycol like acrylic-acid (meta) dipropylene glycol ester (meta), (Meta) A styrene sulfonic acid and sulfopropyl (meta) acrylic ester, The monomer which has a sulfonic group like sulfopropyl (meta) itaconic-acid ester, Polyhydric-alcohol ester of an acrylic acid like acrylic-acid monoglyceride (meta), (Meta) The phosphate of an acrylic acid like monochrome (2-hydroxyl ethyl acrylate) acid phosphate (meta), N-(3-sulfopropyl)-N-METAKU roil amide propyl-N and N-dimethylannmonium betaine, The unsaturated compound of a betaine mold like a 1-(3-sulfopropyl)-2-vinyl pyridinium betaine, Conjugated diene monomers, such as vinylpyridine and its salt, vinyl pyrrolidone, a butadiene, and pentadiene, Halogenation vinylidenes, such as halogenation vinyl, such as a vinyl chloride, and a vinylidene chloride, It is vinyl ester, such as vinyl acetate, acrylonitrile, etc., and one sort chosen from this etc. or two sorts or more are not used together, or, of course, it does not care about using together compounds other than an aromatic series vinyl compound and these aromatic series vinyl compound, either. Furthermore, also making compounds other than the compound mentioned above in the range which does not spoil the object of this invention etc. contain does not interfere.

[0017] Now, it is most suitable for the organic polymer in the constituent in the invention in this application that 25 - 98.9 % of the weight of acrylic-acid (meta) alkyl ester and other vinyl compounds is [ the ethylene system unsaturated compound of others which constitute it ] 0 - 73.9 % of the weight, and the glass transition temperature of this organic polymer is -15 degrees C or more less than 30 degrees C. if it separates from the range of above-mentioned [ the weight rate of these components ], the quantitative ratio of the carboxylic-acid component in an organic polymer and a hydroxyl-group component will fill -- not having -- becoming -- an effect of the invention -- discovered -- hard -- \*\* --

[0018] The glass transition temperature of an organic polymer is -10 degrees C to 15 degrees C still more preferably. The metal finishing coat in which glass transition temperature was formed from the

invention constituent below -15 degrees C is tintured with adhesiveness, and fingerprint-proof nature and abrasion resistance fall, and above 30 degrees C, since membrane formation nature becomes inadequate, it is in the inclination for adhesion with a fingerprint-proof nature metallurgy group front face to fall.

[0019] In adjusting the glass transition temperature of an organic polymer like \*\*\*\*, when it is methacrylic acid methyl, methacrylic acid butyl, methacrylic acid phenyl, etc., glass transition temperature is made to rise, and when the above mentioned acrylic-acid (meta) alkyl ester is a methyl acrylate, an ethyl acrylate, acrylic-acid propyl, butyl acrylate, 2-ethylhexyl acrylate, etc., it can apply the knowledge of dropping glass transition temperature, and can combine suitably.

[0020] Although the organic polymer which combines and has the explained carboxylic acid and hydroxyl group above [ in the constituent of this invention ] needs to be the organic polymer aquosity emulsion (henceforth a carboxylic acid and a hydroxyl-group content emulsion) distributed to stability in the drainage system medium and especially the manufacture approach is not limited, the synthetic approach by the emulsion polymerization in the inside of an aquosity medium is desirable. In this case, in the usual emulsion polymerization, it is common a low-molecular-weight surfactant and to compound more under existence of water-soluble protective colloid, such as a water-soluble polymer of the amount of macromolecules and water-soluble oligomer.

[0021] However, in the emulsion which carried out the polymerization using such a low-molecular-weight surface active agent, mixing stability with the drainage system colloid of the indispensable requirements for configuration b. water solubility chromium compound of this invention and c. inorganic compound is bad, and the problem of a carboxylic acid and a hydroxyl-group content emulsion gelling arises. Moreover, in the emulsion polymerization under water-soluble protective colloid, the reactivity of the carboxylic acid and the hydroxyl-group content emulsion, and the water-soluble chromium compound which were mentioned above is not demonstrated enough, but the chromium elution prevention engine performance becomes inadequate, or the problem to which corrosion resistance falls arises. Then, in composition of the carboxylic acid and hydroxyl-group content emulsion in this invention, it is desirable to use neither the above low-molecular-weight surfactants nor water-soluble protective colloid.

[0022] Then, although the water-soluble usual free radical catalyst (for example, oxidizing agents and azobis system catalysts, such as ammonium persulfate and potassium persulfate) can be used as a polymerization initiator in composition of the invention in this application, the redox system catalyst which used the reducing agent (for example, acid sodium sulfite, sodium sulfite) for the above-mentioned oxidizing agent, respectively is desirable. The amount of this catalyst used is 0.2 - 3.0 % of the weight to monomer AUW, and is 0.3 - 1.5 % of the weight preferably. The composition by the emulsion polymerization in the inside of an aquosity medium should just use the usual approach of combining the various monomers which are constituents so that the glass transition temperature of a polymer may become -15 to 30 degrees C, and trickling them into the above-mentioned initiator and coincidence underwater under stirring conditions. Although it is desirable at this time to make all mix beforehand as for various monomers, it does not interfere, even if it uses the approach of a continuation multistage polymerization or an intermittence multistage polymerization of changing the dropped monomer presentation in time, if needed or uses the polymerization method which trickles independently the monomer from which a property differs.

[0023] Next, although well-known things, such as dichromate, such as chromates, such as a sodium chromate, a potassium chromate, ammonium chromate, chromic-acid magnesium, calcium chromate, chromic-acid cobalt, zinc chromate, chromic-acid manganese, chromic-acid nickel, and strontium chromate, a sodium dichromate, a potassium dichromate, and an ammonium dichromate, and a chromic anhydride, can be used as a water-soluble chromium compound in this invention, it is a chromic anhydride preferably.

[0024] The solid content concentration occupied in the invention in this application in the constituent of invention of the aforementioned carboxylic acid and hydroxyl-group content emulsion is 150g/l. It is above and it is most suitable that the weight rate of a carboxylic acid and hydroxyl-group content

emulsion solid content, and water-soluble chromium compound solid content is within the limits of 60:1-10:1.

[0025] The carboxylic acid in a constituent and hydroxyl-group content emulsion solid content concentration for metal finishing are 150 g/l. When it is the following, the welding of a carboxylic acid and a hydroxyl-group content emulsion is imperfect at the time of desiccation, fixing [ of chromium ] is easy to become inadequate at it, since there are many chromium compounds with the weight rate of a carboxylic acid and hydroxyl-group content emulsion solid content, and water-soluble chromium compound solid content superfluous at 10:1 or more, reactions tend to run short, and also when it is any, chromium elution tightness is not enough.

[0026] Although 60:1 or less are enough as the weight rate of a carboxylic acid and hydroxyl-group content emulsion solid content, and water-soluble chromium compound solid content as for immobilization of chromium, the field of corrosion-resistant ability is not necessarily satisfied enough.

[0027] Next, as drainage system colloid of an inorganic compound, the inorganic oxide particle is distributing to stability in an aqueous medium with the mean particle diameter of 10nm - 50nm, and it is SiO<sub>2</sub> preferably. Colloid and TiO<sub>2</sub> It is colloid.

[0028] Moreover, although one sort chosen from phosphoric acid, polyphosphoric acid, a calcium phosphate, a titanium phosphate, etc. or two sorts or more can be used as an inorganic substance which reacts with an amphoteric metal (typical one is zinc and aluminum), and forms a difficulty water solubility salt, they are phosphoric acid and polyphosphoric acid preferably.

[0029] Moreover, 20:1-1:1 are desirable still more desirable, and the weight rates with the solid content of the inorganic substance which these quantitative relation reacts with the solid content of a carboxylic acid and a hydroxyl-group content emulsion and an amphoteric metal, and forms a difficulty water solubility salt are 15:1-2:1. 30:1-1:1 are desirable still more desirable, and the weight rates of the solid content of a carboxylic acid and a hydroxyl-group content emulsion and the solid content of the drainage system colloid of an inorganic compound are 20:1-2:1.

[0030] Although the inorganic substance which reacts with an amphoteric metal for the desiccation on the processed material front face of an invention constituent and the chemical reaction at the time of welding, and forms a difficulty water solubility salt is an indispensable component When the solid content weight rate of a carboxylic acid and a hydroxyl-group content emulsion, and this component is 20:1 or less, a reaction is inadequate and sufficient immobilization of chromium cannot be performed easily. The case of 1:1 or more has the inclination which adhesion with the surface of metal of the coat formed from the invention constituent worsens, and a problem produces in solvent resistance etc. under the effect of the generated difficulty water solubility salt.

[0031] Moreover, although the drainage system colloid of an inorganic compound is an indispensable component because of immobilization of the manifestation of high corrosion resistance, and chromium, when it is 1:1 or more, the drainage system colloid of a superfluous inorganic compound condenses in the metal finishing film upper part of an invention constituent, and it becomes easy for corrosion resistance to become inadequate when the solid content weight rate of a carboxylic acid and a hydroxyl-group content emulsion, and this component is 30:1 or less, and to produce a problem in fingerprint-proof nature, abrasion resistance, etc.

[0032] When fixed period storage needs to be carried out in mixing (mixing) of an invention constituent until it is used for metal finishing, it is desirable to save independently a carboxylic acid and a hydroxyl-group content emulsion, and a water-soluble chromium compound, for example, a chromic anhydride, or a chromic anhydride water solution, and to mix both from the point of the stability of liquid and the durability of the engine performance, at the time of an activity. About the inorganic substance which reacts with the drainage system colloid of an inorganic compound, and an amphoteric metal, and forms a difficulty water solubility salt, whichever it mixes and saves by the side of a carboxylic acid and a hydroxyl-group content emulsion, and a water-soluble chromium compound water solution, interfere and there is nothing.

[0033] Thus, the constituent for metal finishing of invention which was saved and was prepared in the activity can be applied to the front face of various metals (iron, zinc, zinc galvanizing, aluminum, etc.)



according to the usual approach, and the target metal finishing can be performed by subsequently drying. Although especially spreading thickness is not limited by the metaled surface state, selecting in the range which does not spoil weldability is desirable, and 0.3micro - 3.0micro of average thickness after desiccation is 0.3micro-1.0micro desirably. Desiccation can apply the desiccation conditions of usual spreading mold KUROME-TO, and there is what will be limited especially if only the heating value in which moisture evaporates is given. [ no ]

[0034] Thus, since the processed metal comes out as it is and it has sufficient chromium elution tightness, corrosion resistance, and fingerprint-proof nature, it is useful also for the application which does not apply top coat, such as home electronics, and when performing spreading and electrodeposition of a coating in piles upwards, the outstanding coating adhesion is discovered.

[0035]

[Function] Although it has come to solve enough the reason to which the constituent for metal finishing of the invention in this application explained in full detail above solves the conventional technical problem, holds high corrosion resistance, and could also prevent elution of chromium, it is considered to be in general as follows. Namely, balance of the amount of specification [ combine a carboxylic-acid radical and a hydroxyl group in the same copolymer molecule, and / an owner \*\* polymer ] of both radicals called a carboxylic acid and a hydroxyl-group content emulsion, as having whenever [ little / of the steric hindrance between both the radicals of the level which cannot reach at all /, and advanced access ], and \*\*\*\* in mixing of a carboxylic-acid radical content polymer and a hydroxyl-group content polymer At the time of the desiccation and welding at the time of being used for a surface of metal, the chemical reaction of the kind which it is between the water-soluble chromium compounds which live together is caused.

[0036] As a result, probably, immobilization of chromium is performed between carboxylic-acid radicals, and it is thought that the hydroxyl group has achieved one sort of catalyses in the sense of a wide sense in that case. And elution gives very little engine performance.

[0037]

[Example] Although an example is given to below and this invention is concretely explained to it, this invention is not limited at all by the publication of these examples in the range.

[0038] (1) The synthetic deionized water 400 section of a carboxylic acid and hydroxyl-group content emulsion A-E (the weight section is shown.) the following -- being the same -- A-E which it puts into a reaction vessel, and 60 degrees C is raised whenever [ solution temperature ], and is shown in a table 1 at this -- with the monomer mixture 400 weight section of each copolymerization rate After being dropped stirring so that the liquid which dissolved the ammonium persulfate 4 section in the deionized water 96 section, and the liquid which dissolved the acid sodium sulfite 11 section in the deionized water 89 section may be ended to a concurrency in 2 hours, The carboxylic acid and hydroxyl-group content emulsion No.A-E which performs a polymerization reaction and fills this invention were compounded stirring at 60 degrees C succeedingly for 3 hours. Moreover, emulsion No.F-G which separates from this invention as an example of a comparison was similarly compounded at a monomer copolymerization rate shown in a table 1.

[0039]

[A table 1]



No	共重合割合（重量％）				有機重合 体ガラス 転移温度	備 考
	TGの高い 単量体	TGの低い 単量体	カルボン酸 含有単量体	水酸基含 有単量体		
A	MMA= 20 St = 20	BA= 47	MAA= 5	HEA= 8	4℃	実施例
B	St = 35	BA= 49	MAA= 5	HEMA= 11	2℃	
C	MMA= 42	BA= 45	MAA= 5	HEA= 5 GMA= 3	7℃	
D	St = 34	BA= 46	MAA= 4	HEA= 16	-5℃	
E	MMA= 53	BA= 31	MMA= 5	HEMA= 11	32℃	
F	St = 45	BA= 50	MAA= 5		5℃	比較例、水酸 基を有しない
G	MMA= 17 St = 15	BA= 45	MAA= 13	HEA= 10	6℃	比較例 MAA 過剰
TG =ガラス転移温度 MMA =メチルメタアクリレート St =スチレン MAA =メタアクリル酸 HEA =アクリル酸2-ヒドロキシエチル HEMA =メタアクリル酸2-ヒドロキシエチル GMA =グリシジルメタアクリレート BA =ブチルアクリレート						

[0040] (2) It mixed with the drainage system colloid of a water-soluble chromium compound and an inorganic compound, and the inorganic substance (difficulty water solubility salt plasticity inorganic substance) which reacts with an amphoteric metal and forms a difficulty water solubility salt, the constituent for metal finishing to examples 1-5 was prepared, and the engine performance was evaluated so that it might become the solid content concentration and the mixed rate which show mixing of the constituent for metal finishing, and the carboxylic acid and hydroxyl-group content emulsion No.A-E of the performance-evaluation above in a table 2.

[0041]

[A table 2]

No.	調合物／混合割合（固形分比）					組成物中有機重合体固形分濃度（g／ℓ）
	有機重合体	水溶性クロム化合物	無機化合物の水系コロイド	難水溶性塩形成性無機物		
実施例	1	A／10	CrO <sub>3</sub> ／0.6	SiO <sub>2</sub> ／ 2	磷酸／ 1	200
	2	B／10	CrO <sub>3</sub> ／0.5	SiO <sub>2</sub> ／ 1	磷酸／ 2	200
	3	C／10	CrO <sub>3</sub> ／0.4	SiO <sub>2</sub> ／ 2	磷酸／ 0.8	200
	4	D／10	CrO <sub>3</sub> ／0.6	SiO <sub>2</sub> ／ 1	ポリ磷酸／2	200
	5	E／10	CrO <sub>3</sub> ／0.6	SiO <sub>2</sub> ／ 2	磷酸／ 1	200
比較例	1	F／10	CrO <sub>3</sub> ／0.6	SiO <sub>2</sub> ／ 2	磷酸／ 1	200
	2	G／10	CrO <sub>3</sub> ／0.6	SiO <sub>2</sub> ／ 2	磷酸／ 1	200
実施例	6	A／10	CrO <sub>3</sub> ／0.6	SiO <sub>2</sub> ／ 2	磷酸／ 1	120
	7	A／10	CrO <sub>3</sub> ／1.5	SiO <sub>2</sub> ／ 2	磷酸／ 1	200
	8	A／10	CrO <sub>3</sub> ／0.4	SiO <sub>2</sub> ／ 0.2	磷酸／ 1	200
	9	A／10	CrO <sub>3</sub> ／0.6	SiO <sub>2</sub> ／ 12	磷酸／ 1	200
	10	A／10	CrO <sub>3</sub> ／0.6	SiO <sub>2</sub> ／ 2	磷酸／ 0.3	200

[0042] Moreover, as an example of a comparison, the performance evaluation also of the constituent for metal finishing using emulsion No.F-G which separates from this invention (examples 1-2 of a comparison) and the constituent for metal finishing of a carboxylic acid and hydroxyl-group content emulsion solid content concentration (example 6) which separates from the optimal recommendation range of this invention, and the constituent for metal finishing (examples 7-10) with which a mixed rate separates from the optimal recommendation range was created, combined and carried out, and, similarly the result was written together to a table 2.

[0043] The constituent for metal finishing obtained in this way evaluates the following engine performance by making into a sample what applied to 0.6mm thickness galvanized steel sheet (Japanese test panel company make) the shelf test which comes out as it is, and all in the No.3 bar coating machine, and dried them for 10 seconds in 200-degree C ambient temperature, and shows a result in a

table 3.

[0044] The atomic absorption spectrophotometry of the chromium metal eluted after a DIP and in liquid for 5 minutes in the sample plate was carried out to alkaline-degreasing liquid (Pyroclean442 made from 3 \*\*\*\*\* Co.) of 50 degrees C of chromium elution tightness, and weight % to the surface treatment coat Nakakane group chromium before a DIP estimated. The semantics of a notation is as follows.

O : Chromium elution Less than [ 5% ] O: Chromium elution 5% - 15%\*\* : 15% of chromium elution -, 30%x: 30% or more of chromium elution [0045] The spray of the brine was carried out to the corrosion-resistant sample plate at 35\*\*1 degree C 5% for 400 hours, and the area of the generating condition of the rust estimated. The semantics of a notation is as follows.

O : White rust generating 0%O: White rust generating 0%- 5%\*\* : White rust generating 5% - 20%x: White rust generating 20% or more [0046] Vaseline was applied to the fingerprint-proof nature sample plate, and the color difference before and behind spreading estimated. The semantics of a notation is as follows, and it cannot so be overemphasized that there is little color difference that fingerprint-proof nature is excellent.

O : Color difference \*\*E Less than [ 0.5 ] O: Color difference \*\*E 0.5-1.0\*\* : Color difference \*\*E 1.0-3.0x: Color difference \*\*E 3.0 [0047] or more The area which applied the melamine alkyd coating (GURIMIN[ by Shinto Paint Co., Ltd. ] # 100) to the top coat adhesion sample plate at 30micro thickness, was dried for 30 minutes in 120-degree C ambient temperature, and exfoliated in 1mm base eye friction test estimated. The semantics of a notation is as follows.

O : Paint-film-exfoliation-less O: Paint film exfoliation - 5%\*\* : Paint film exfoliation 5% - 20%x: Paint film exfoliation 20% or more [0048] They are 500 g/cm2 to an abrasion resistance sample plate. The both-way rubbing test by cheesecloth No.3 was performed 100 times under the load, and macro-scopic observation of the desquamative state of a paint film estimated. The semantics of a notation is as follows.

O: [ ] abnormalities-less \*\*: a little -- paint film exfoliation x: Paint film exfoliation [0049] Liquid ammonia quality of a metal finishing constituent (shelf test)

The prepared metal finishing constituent was kept to 25-degree-C65%RH, and the days in which an abnormal occurrence is not accepted estimated. The semantics of a notation is as follows.

O: [ ] more than five day \*\*: One day - five day x: Less than one day [0050]

[A table 3]

No.		表面処理金属サンプル性能					金属表面処理 用組成物の安 定性
		クロム溶 出防止性	耐蝕性	耐指紋性	耐磨耗性	上塗り塗 料密着性	
実 施 例	1	◎	◎	◎	○	◎	○
	2	◎	◎	◎	○	◎	○
	3	◎	◎	◎	○	◎	○
	4	◎	◎	◎	○	◎	○
	5	○	○	△	△	◎	△
比 較 例	1	×	◎	○	×	◎	○
	2	○	△	×	×	◎	○
実 施 例	6	○	○	○	△	◎	△
	7	△	◎	○	○	◎	△
	8	△	○	◎	○	◎	○
	9	○	◎	△	△	△	△
	10	△	△	○	○	◎	○

[0051] It turns out that the constituent for metal finishing which fulfills examples 1-5, i.e., the terms and conditions of this invention, from a table 3 is equipped with the outstanding chromium elution tightness, corrosion resistance, and many other properties. There is no item which projects and is excellent, and the example 5 also equips fingerprint-proof [\*\*\*\*] nature etc. with the property which is imperfection and which maintained \*\*\*\* balance, although it is however. On the other hand, since the organic polymer emulsion in this invention does not contain a hydroxyl group, preventing elution of chromium cannot be finished, and in the example 2 of a comparison, since there are too many amounts of carboxylic acids, it is inferior to fingerprint-proof nature and abrasion resistance with the example 1 of a comparison.

[0052] Next, although examples 6-10 have separated from the optimal recommendation condition range which makes the highest engine performance of the invention in this application discover, they show the property by which \*\*\*\* balance was carried out. For example, 7 and 9 are excellent in corrosion resistance, and examples 6 and 10 are [adhesion / with top coat] excellent in 8 at fingerprint-proof nature, respectively. It turns out that the constituent for metal finishing applied to this invention from the

above example and the example of a comparison has discovered the outstanding property by joint adoption of the component.

[0053]

[Effect of the Invention] The invention in this application which explained in full detail above does so the effectiveness of the prevention engine performance and the high corrosion-resistance ability of chromium elution which reacts with the drainage system colloid of the carboxylic acid and the hydroxyl-group content emulsion of a presentation of a. specification, b. water-solubility chromium compound, and c. inorganic compound, and d. amphoteric metal, and forms a difficulty water-solubility salt and which was not conventionally attained by joint adoption of four requirements for an indispensable configuration of an inorganic substance that it is discovered on both the level with which can be satisfied of the opposite engine performance.

[0054] Therefore, in the invention constituent of this application, there is also no need of taking into consideration environmental pollution, a chromium recovery system, etc., and the metal finishing of low cost also of construction became easily possible. It is also one of the effectiveness that it is what satisfies enough the fingerprint-proof nature and top coat adhesion which are required of the processing coat other than chromium elution tightness or high corrosion resistance, of course, abrasion resistance, etc. and the neglect stability of this constituent itself, and not to require that it is high and special to storage of a constituent etc.

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[Translation done.]